Elimination of Cadmium from wastewater using modified and unmodified tea waste in Kisii County, Kenya

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ABSTRACT

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|  The problem of poor water quality in Kenya is increasing as a result of pollution of water systems due to discharge of effluents from industrial and agricultural activities, mining action and land dumping of urban waste. Most rural populations in Kisii County generally depend on traditional methods such as filtration to treat the water. In order to eliminate Cadmium (II) ions from waste water, the study evaluated the adsorption approach using tea waste as an environmentally friendly and locally accessible adsorbent using both modified and unmodified biomass tea waste. Sulfuric acid treatment of biomass tea waste improved its efficacy in this study. Initial metal ion concentration, contact time, pH, and sorbent mass were among the parameters that were examined. The experiment's findings showed that 0.7 grams of sorbent mass and 70 mg/l of initial metal ion concentration were ideal values. 95 minutes of contact time and a pH of 6. The metal ion concentration was ascertained using AAS. FT-IR analysis of the biomass tea waste showed the presence of O-H at a maximum of 3395 cm-1, COO- at a maximum of 2448 cm-1, C=O at a maximum of 1594 cm-1, and P-OOH at a maximum of 1216 cm-1. This study show that both modified and unmodified tea waste can be applied to eliminate Cadmium from waste water |

*Keywords: adsorption; concentration; functional groups; heavy metal*.

1. INTRODUCTION

Water is a necessary component of life and has a major effect on environmental and public wellbeing in addition to being the basis for the majority of our economic endeavors. According to the United States Public Health Service (USPHS), contaminated water is defined as having any kind of external material, (natural and artificial) radioactive, or biological) that has the tendency to lower the water's quality to the point where it becomes dangerous. Since they have elevated concentration of poisoning.and threat to both humans and animals, heavy metals are the primary environmental contaminants (Amarasinghe and Williams, 2007). Numerous pathways allow contaminants to enter the systems, including mining operations, residential wastewater, and runoff from agriculture. This increases the amount of species that are metallic discharged into the ecosystem (Churong *et al.,* 2013).

According to WHO recommendations, drinking water can have a cadmium concentration of up to 0.003 mg/L. Cadmium is regarded as a very hazardous metal with no recognized biological purpose, The most common method Cadmium exposure occurs in human is through consuming a product that contains cadmium. Another method that individuals can be exposed to cadmium is through cigarette smoking, burning garbage, and burning fossil fuels (new bigging *et al*., 2015). Excessive levels of cadmium within the human body might result in infertility, immune system damage, mental illnesses that cause abnormalities in the mind, and stomach pain (Mohod and Dhote, 2013)

The buildup of cadmium throughout the human body, particularly in the kidneys, can result in kidney dysfunction, high blood pressure, liver disease, severe lung damage, and damage to the brain and nerves are just a few of the detrimental health impacts that can result from excessive cadmium exposure, Alopecia anaemia, emphysema, learning disabilities, headaches, development retardation, and arthritis are some of the symptoms (Sathish *et al*., 2014).

It has been determined that cadmium (Cd) is an extremely hazardous heavy metal (Ferreira *et al.,* 2012). Cadmium has lately surpassed lead and mercury as the most hazardous heavy metal that causes harm to the health of people and the surroundings because of its acute toxicity (kumar *et al.,* 2014). Diarrhea, pulmonary edema, weakness, nausea, vomiting, and headaches are all signs of acute poisoning. Dust from mulberry wood treated with HCI acid has been used to study the biosorption of cadmium on aqueous solution (Shah *et al.,* 2011). Exposure to heavy metals over recommended levels in humans can cause kidney damage, reported in Kenya (Nyaboke *et al.,* 2017).

Heavy metal ions may be removed from solutions in water using several methods related to chemical, biological, and physical processes (Kumar *et al.,* 2014). Chemical oxidation, disinfection, ion exchange, sedimentation, adsorption, electrolysis, filtration, solvent extraction, coagulation, foam flotation, and chemical precipitation are a few of these processes (Hossain *et al*., 2012). High initial cost linked to other technologies as reverse osmosis, ultra filtration, and nano-filtration (Miretzky et al., 2006).The high cost of this conventional physicochemical methods has prompted increasing interest in conducting research on employing low-cost alternative mechanism and one of the methods is adsorption by using alternative low cost adsorbents has been found to be economically viable, This method is convenient, easy operation, simple in design, ecofriendly in nature and has excellent performance (Ahmad and Kumari 2010).

Many inexpensive adsorbents have been selected based on their ability to obtain heavy metals from water For this reason, adsorption has been used as a less expensive technique of treating water (Amit and Monocha, 2006). However, no concrete research on the use of biomass tea waste treated with sulphuric acid as low cost absorbent in heavy metal removal from wastewater has been conducted in major Counties such as Kisii which is experiencing rapid growth of industries especially in the agricultural sector. Therefore, there was need to look for alternatives adsorbent which are reliable and ecofriendly and hence the need to use tea waste in our study as a possible strategy.

**2.0 MATERIALS AND METHODS**

 **2.1 Reagents and Chemicals**

All of the reagents and chemicals utilized had analytical quality. (Purity > 98.9%) . Every solution was made using double-distilled water. 0.1 Sodium Acetate was used to create metal solutions in order to keep the ionic strength consistent. Soluble metal salt of Cd2+ and as well as KNO3, NaOH, HCl, H2SO4, sodium acetate, sodium bicarbonate and potassium bromide were among the chemicals used and were commercially purchased from PYREX East Africa limited with its branch located in Nairobi Kenya.

**2.2 Standard solution and stock solution preparation**

Cd2+ stock solutions with concentrations of 1000 ppm was made from the corresponding salts. Distilled water in a 1000 ml volumetric flask was utilised to dissolve 1.8759g of Cd (NO3)2.5H2O, to create the stock solution. Using commercial buffer tablets (pH 4 and 7) and a pH meter (model Hanna GLP 110), the model solution was made with the necessary metal ions under investigation and adjusted to 5.0. Acetic acid and sodium acetate were used to make the acetate buffer, and distilled water was added to the solutions until they reached the 1000 cm-3 level. To create each working solution, Distilled water was used to dilute the stock solutions to the appropriate concentration.

**2.3 Preparation of the adsorbent**

After being locally gathered from the Nyamache tea factory in Kisii County, the tea trash was taken to the Jomo Kenyatta University of Agricultural and Technology labs, where it was extensively cleaned using deionized water and then allowed to dry to remove moisture in an oven preheated to 105°C, then sieved and ground into a fine powder and separated into two parts. One section was handled with 1M sulfuric acid in a 1:2 weight-to-volume ratio, the mixture was heated to 150° C for 24 hours to get rid of the residue. After cooling distilled water was used to rinse each product to get rid of extra acid, and then left in NaHCO3 (1%) for the entire night (Moyo and Chikazaza, 2013). The modified tea waste was then dried to a consistent weight at 105° C. The resultant powders, which were stored in desiccators ready for use, were marked as MTW (modified tea waste) and UTW (unmodified tea waste).

## **2.4 Surface Characterization**

FTIR spectra using the SHIMADZU FTIR 8400S (Kyoto, Japan) was used to characterize the functional groups found in tea trash. I mg of dried tea waste material, both treated and untreated, was combined with 50 mg of KBr (1:50) to create the FTIR analysis samples. After that, the mixture was vacuum-pressed after being finely powdered into a pellet. An FTIR spectrophotometer was then used to analyze the pellet. The measurement range for the adsorbents' spectra was 600–4000 cm-1. Prior to and following acid treatment, spectra were plotted on the absorbance axis using the same scale.

**2.5 Sem Analysis**

The texture and surface morphology of the both MTW and UTW was determined using the Scanning Electron Microscope.

**2.6 Instrumentation**

An air-acetylene flame Shimadzu AAS Model AA 7000, a spectrophotometer for flame atomic absorption was used to test Cd2+. To determine how the pH impacted the adsorption of metal ions, a pH meter (pH 211, Hanna instruments) was utilized to record the pH. The organic functional groups in tea debris that were in charge of the adsorption of heavy metal ions were detected using a Fourier transform infrared spectrophotometer (Shimadzu, Japan, Model FTS-8000). The metal adsorption was measured using an atomic absorption spectrophotometer. A mechanical shaker and Scanning Electron Microscope were also employed.

**2.7 Adsorption studies**To assess the effectiveness of utilizing modified tea waste and unmodified tea waste to remove cadmium from aqueous solutions, batch tests were conducted. For these materials, the primary factors influencing bio-sorption, including adsorbent dose, initial metal concentration, pH and contact time were assessed. The stock solution was a cadmium metal standard at 1000 mg/l. To create each working solution, the stock solutions were diluted with distilled water to the appropriate concentration.

The sorption results were used to calculate the metal uptake from modified and unmodified tea trash. $ Q\_{e}=\frac{\left(c\_{i}-c\_{o}\right)V}{M}$………………………………………………………………….2.1

where Ci and Ce are the initials and equilibrium metal concentrations, and qe is the metal absorption (mg metal adsorbed per g adsorbent). M is the mass of the dried adsorbent utilized, and V is the reaction mixture's volume (Moyo and Chikazaza 2013).
Pb (II), Cd (II), and Cu (II) removal percentages (R%) in solution were calculated.

$R\% =\frac{Co-Ce}{Co}×100$……………………………………………………………2.2

Where Co and Ce are the initial and equilibrium metal concentrations.

The significance of the data was ascertained using statistical analysis employing ANOVA.

**3. Results and discussion**

The adsorbents' surface appearance and texture were assessed using SEM, and the functional groups in charge of adsorption were examined using FTIR. The effects of the initial metal ion concentration, pH of the solution, contact time, and adsorbent dosage were examined. The findings were presented as the removal effectiveness (% Removal) of the adsorbent.

**3.1 Surface characterization of biomass tea waste**

Figure 1 illustrates the surface appearance and texture of the tea waste adsorbent as shown in the SEM images. Figure 1 illustrates the tea waste's sluggish rough and restrictive surface before H2SO4 treatment. However, as can be observed in fig. 1(b), the biomass tea waste developed distinct pores following treatment with sulfuric acid. The partial breakdown of hemicellulose, cellulose, and lignin brought on by sulfuric acid treatment may be the cause of the morphological changes in the biomass's structure. The adsorption capabilities of the acid-modified tea trash improved as a result of these morphological alterations. (Nthiga *et al.*, 2016). showed similar outcomes with acid-treated orange peel and avocado seed.



(a)



(b)

**Fig 1: SEM images for (a) UTW (b) MTW**

The existence of the isolated silanols was the cause of the weak absorption bands at Vmax 3885cm-1 for both MTW and UTW (Huang Ma Zhao and (2015). It was determined that the significant absorption bands at Vmax 3392cm-1 of UTW and 3392cm-1 of MTW, respectively, were caused by the hydroxyl groups' stretching vibration when OH was present. For both MTW and UTW, It was discovered that the existence of C=O stretching vibrations was the origin of the absorption band at Vmax 1645 cm-1. (Sych *et al.,* 2012).

The amine group stretching vibrations were suggested by the peak at Vmax1552cm-1 for both MTW and UMT. Both MTW, and the peaks seen at 1413 cm-l ascribed to the –COO-l groups (Nikhil and Bhalerao). For both modified and unmodified tea waste, the band at Vmax1255 cm-1 was connected to the hydrogen-bonded P-O and O-C stretching mode, which are seen in P-O-C and P-OOH. The chemical change may be the cause of the new peak's emergence at 1106 cm-1 (Godlewska *et al.,*2018. The peaks' shifting indicates how the metal ions and the hydroxyl group on the on the biomass's surface interact chemically (Nthiga *et a l*.,2016). The ionized linkage P-O- which was present in esters and phosphate was linked to the band at Vmax 1106 cm-l for acid-treated tea waste. It was also attributed to symmetric vibration in P-O-P. While the peak at Vmax 753cm-l was linked to in-plane ring deformation



 **Figure2: FTIR spectra of unmodified and modified tea waste adsorbent**

**3.2 Optimization experiments**

**3.2.1 Effect of pH**

The pH still plays a big role in the removal of metal ions because it affects the chemistry of the solution and the surface properties of the adsorbent. Figure 3 shows how pH affects the percentage of cadmium ions removed. By raising the pH of the solution from 2 to 6, the adsorption of cadmium on the MTW and UMTW is considerably impacted. The percentage of metal ion removal rose between pH 2 and pH 6, after which it started to fall. The result show that UTW had a maximum sorption of pH 5.9 while MTW had a maximum adsorption of pH 6.0. maximum adsorption at pH 4.5 was reported (Signh *et al.,* 2012). in raw and acid-treated maize tassel, pH 4.2 and pH 6.1 have been reported (Mwangi *et al*., 2012).

The percentage removal of Cd (ll) ions increased to a maximum of pH 5.9 and 6.0. Further pH increases resulted in a decrease in adsorption in both MTW and UTW. At a low pH, the protonation of the functional groups is intimately related to the adsorbent's surface. The formation of cadmium hydroxide starts when the pH rises over 6.0. This prevents the ions of the metal from circulating and renders them unavailable for the purpose of adsorption, precipitation affects the adsorption process. These results are also in line with earlier adsorption research that found a pH range of 4 to 5 pH for Cd (ll) ions removal by a variety of adsorbents (Samadi *et al.,* 2014).

**Fig 3: Effect of pH on adsorption of Cd2+ on UTW and MTW**

**3.2.2 Effect of contact time**

 At first, the adsorption of Cd2+ increased quickly up to equilibrium time for both MTW and UMT; after the elimination percentage was almost steady this time signifying the achievement of equilibrium conditions, as seen in figure 4. Figure 4 demonstrates that for both MTW and UTW, the maximum adsorption of 75.2% was reached in the first 85 minutes and 96% in the 95 minutes. The agitation time measured in this study i compared to that which Benard and Jimoh (2013) reported using orange peel, but it is comparable to that which was disclosed by (Banarjee *et al*., 2012) on the investigation of lead adsorption by the peel of a watermelon. this is explained by variations in the adsorbent's nature and experimental conditions and procedures.

**Fig 4: Effect of contact time** **on adsorption of Cd2+ on UTW and MTW**

**3.2.3 Effect of adsorbent dosage**

The effect of adsorbent dosage on removal of Cd2+ ions was conducted and the outcome recorded in figure 5. The findings in Figure 5 demonstrate that the dosage of the adsorbent affected the absorption of cadmium (II) ions. When the mass of the adsorbent rises, the uptake of cadmium (II) ions increases as well, reaching a maximum of 84.3% and 93.5% for UTW and MTW, respectively. The improved surface texture and micropore structure following acid modification were responsible for the observed increase in percentage removal as shown in the figure 5 increasing the ions' ability to enter the adsorption sites (Anwar *et al.,* 2010).

**Fig 5: Effect of mass of the biomass on adsorption of Cd2+ onto UTW and MTW**

**3.2.4 Effect of initial metal ion concentration**

 Figure 6 illustrates the considerable impact of the initial concentration of metal ions in aqueous solution on the adsorption of ions on UTW and MTW.The findings indicate that the absorption of Cd ions was lower in UMW than in MTW. This demonstrates that the acid treatment improved the metal ion sorption up to a maximum of 98.2 % for MTW and 97% for UTW. The profile of Cd2+ sorption was shown to rise as the initial metal concentration increased. This work yielded higher result than a study on the adsorption of copper (II) ions using raw banana peel, which found 88% at 10 mg/L, 5 g (Hossain *et al.*, 2012).

 **Figure 6: Initial Cd2+ ions concentration on adsorption by UTW and MTW**

**Conclusion**

 In this study, sulfuric acid was used to chemically modify biomass from unmodified tea waste (UTW). An an increase in the shifted functional groups' number (MTW) for Cd2+ ion adsorption was revealed by the FTIR spectra's more strong peaks. The biomass tea waste developed distinct pores following treatment with sulfuric acid. The partial breakdown of hemicellulose, cellulose, and lignin brought on by sulfuric acid treatment may be the cause of the morphological changes in the biomass's structure. Adsorbent dosage, contact time, pH, and initial metal ion concentration all had a significant impact on the adsorption process. For the UTW and MTW removal of Cd2+ from wastewater, MTW displayed highest percentage removal for all the parameters under investigation.

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 **APPENDICES**

## **Appendix 1: Variation (ANOVA) for the effects of pH for Cd (II) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | SS | DF | MS  | F | P-Value | F- Critical |
| **Between Groups** | **178.846** | **1** | **163.837** | **85.48** | **1.8E-10** |  |
| **Within Groups** | **63.395** | **36** | **19.167** |  |  | **4.11** |
| Total | 242.2412 | 37 |  |  |  |  |

## **Appendix 2: Variation (ANOVA) for the effect of sorbent mass for Cd (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | SS | DF | MS  | F | P-Value | F- Critical |
| **Between Groups** | 1.8986 | 1 | 1.8986 | 54.87 | 1.3-08 |  |
| **Within Groups** | 0.9345 | 35 | 0.0346 |  |  | 4.12 |
| Total | 2.8331 | 36 |  |  |  |  |

## **Appendix 3: Variation (ANOVA) for the effect of contact time on Cd (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Between Groups | 28076 | 1 | 28076 | 65.7 | 1.7-10 |  |
| **Within Groups** | **9768.345** | **41** | **427.3416** |  |  | **4.07** |
| Total | 37844.345 | 42 |  |  |  |  |

## **Appendix 4: Variation (ANOVA) for the effect of initial metal ion concentration on Cd (ll) ions removal**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source of variation  | SS | DF | MS  | F | P-Value | F- Critical |
| Between Groups | 1472.34 | 1 | 1472.348 | 80.256 | 2.4-10 |  |
| Within Groups | 698.578 | 32 | 18.3456 |  |  | 4.15 |
| Total | 2170.926 | 33 |  |  |  |  |